CRACKING PROPERTIES OF SAPO-37 AND FAUJASITES

M. BRIEND, A. LAMY, D. BARTHOMEUF, Laboratoire de Réactivité de Surface et Structure, URA 1106, Université P. et M. Curie, 4 place Jussieu, 75252, Paris Cédex 05.

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Abstract :

SAPO-37 materials with Si atomic fraction from 0.12 to 0.22 are studied for their thermal stability, their acidity and their cracking activity. Most of the acid sites have a medium acid strength. A very small number of sites is very strong. The materials are thermally stable up to high temperatures. After pretreatment at 1175 K they are as active as an ultrastable faujasite in the cracking of n-octane.

IINTRODUCTION

SAPO-37, isotype of faujasite, is an active catalyst for cracking reactions (1,2). The present paper compares the properties of this material with those of faujasites.

EXPERIMENTAL

The samples are synthetised as described in (3) for sample Si-0.12 and Si-0.13 and in (4) for the other solids. The chemical analysis gives results in table 1.

XRD is used to determine the unit cell parameter of the as-synthetised samples. The heating chamber of a Guinier Lenné camera is employed to follow the changes in crystallinity and to determine the temperature for the loss of crystal structure.

TPD of NH_3 is followed using a quadrupole mass spectrometer Quadruvac PGA 100 Leybold-Heraeus.

The desorption of pyridinium ions from the H-SAPO-37 samples is followed by infrared spectroscopy.

The catalytic activity in the cracking of n-octane at 725 K is studied in a microreactor with H_2 as carrier gas.

RESULTS AND DISCUSSION

Si incorporation in the framework

The incorporation of Si in the SAPO-37 framework is seen by the decrease of the unit cell parameter a_o (table 1) as the materials contain more Si.

The mechanism II of of substitution of Si for P in a theoretical $AlPO_4$ framework creates isolated Si atoms (1). Each Si atom generates one proton. According to mechanism III, 2 Si replace a pair Al-P in the $AlPO_4$ framework. In the case of SAPOP-37, Si containing islands are formed (2-5,7). This decreases the potential number of protons formed if no Al is included in those Si islands (5). Alternatively some Si-Al faujasite phase has been described (2,7). The table 1 shows that the Al fraction is often less than the theoretical value 0.50 which suggests the existence of Si islands. The difference from 0.50 increases as the Si content rises (except for the sample Si-0.20 which in fact contains some impurities of SAPO-20). This corresponds to an increasing amount of Si in islands. This is confirmed by the simultaneous decrease in the amount of occluded template (table 1) which indicates that a smaller number of charges have to be neutralized.

Thermal stability

The stability of the crystal structure studied in the heating XRD chamber is very high (table 1). In a flow of dry O_2 or of oxygen saturated with water at room temperature the structure collapses near 1200-1300 K which is similar to the case of the ultrastable LZY-82 zeolite (8). Nevertheless the SAPO-37 structure is not stable in ambient conditions for the template free samples (table 2). The instability occurs when the template free sample is contacted with water at temperatures lower than around 350 K. It probably results from the attack of Al-O-P bonds (8).

Acidity

The TPD of ammonia and of pyridine (table 3) gives one broad peak for all the SAPO-37 materials (free of template) located near 500 K or 665 K for the two bases respectively. Examples are given for Si-0.13 and Si-0.20 in table 3. The same experiment gives for HY and for a dealuminated sample (HYD) 2 peaks indicating two main average acid strength distributions. The mean acid strength of SAPO-37's is intermediate between the two which exist in faujasites (9). A detailed infrared study of the acid strength of protons followed by the limit temperature to evacuate the pyridinium ions shows (table 3) that higher temperatures are required (i.e. stronger acid present) for the SAPO-37 material than for HY or even than the dealuminated HYD compared to Si-0.13. This suggests the presence of very strong acid sites which infrared study showed to be in a very small amount (6).

The TPD peaks related to the medium acid strength which is the main source of acidity very likely reflects the protonic acidity associated to isolated Si-O-Al species. The very strong sites evidenced by infrared would be the Si-O-Al centers at the border of Si islands.

CATALYTIC ACTIVITY

The n-octane cracking carried at 725 K gives the results of table 4. After a pretreatment at 875 K for SAPO-37 and 675 K for HY (in order to avoid structure collapse) the % conversion and selectivities are reported in table 4. The very active HY had to be tested at a higher flow rate in order to decrease the % conversion to the SAPO's range. With a similar flow rate HY would be 15 to 20 times more active. The table 4 shows that similar products are formed with all the catalysts. Looking at the ratios olefin/paraffin, values of 1.9, 1.9 and 1.6 are obtained for Si-0.16, Si-0.20 and Si-0.22 while HY gives 1.2. This suggests lower hydrogen transfer reactions for SAPO's which might result from a higher distance between close sites than in Si-Al faujasites. For the branched to non branched hydrocarbons ratios, SAPO's give 0.6, 0.5 and 0.6 in the same order of materials as above and HY 0.65.

Increasing the pretreatment temperature up to 1225 shows that HY looses its activity near 1075 K and the SAPO's together with the ultrastable LZY-82 material near 1175 K. The table 5 compares the changes in per cent conversion for Si-0.22 and LZY-82. It shows that after pretreatment at 1175 K Si-0.22 is even more active than LZY-82. This stability for the catalytic properties at high temperatures may be related to the high thermal stability described above in tables 1 and 3.

In conclusion the main influence of phosphorus in SAPO's compared to Si-Al faujasites is an increased thermal stability which maintain catalytic properties after heating at high temperatures. It also give rise to a higher olefin to paraffin ratio suggesting a lower hydrogen transfer activity.

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Table 1. Characteristics of SAPO-37 materials

	Si 0.12	Si 0.13	Si 0.16	Si 0.20	Si 0.22
Si_x (a)	0.12	0.13	0.16	0.20	0.22
Al y	0.50	0.49	0.48	0.50	0.46
Pz	0.38	0.49	0.36	0.30	0.32
Occluded templates % (b)	22.3	20.7	21.9	19.7	18.5
a_o (Å) (c)	24.76	24.76	24.74	24.70	24.71
Thermal stability (O_2) (K)	nd (d)	1270 ± 30	nd	nd	1320 ± 30
O_2 + H_2O (K)	nd	1275 ± 30	nd	nd	1240 ± 30

a : x, y, z molar fraction
b : weight %
c : as-synthetised samples
d : not determined

Table 2. Thermal stability

With template	stable		template decomposition	stable
template free no water		stable		
template free + water	unstable	stable		
	RT	~ 350 K	~ 850 K	1200-1300 K

Table 3. Acidity of SAPO-37 materials

	TPD NH_3	TPD Py	T desorption pyridinium
Si-O.13	500 (a)	665 (b)	723 (c)
Si-0.20	500	665	673
HY	455 520	545 735	623
HYD	455 520	545 735	673

a, b peak (K) of the maxima in TPD of ammonia (a) or pyridine (b)

c evacuation temperature (K) for the complete disappearance of the pyridinium ion (infrared spectroscopy)

Table 4. Selectivities (mole %) in the cracking of n-octane at 725 K

Products	Si-0.16(a)	Si-0.20	Si-0.22	HY (a)
methane (b)	4.4	3.9	3.8	3
ethylene (b)	2.8	2.2	2.1	1.7
ethane	7.9	5.9	6.7	4.7
propene + propane	24.8	23.0	24.9	25.4
iso-butane	3.1	5.2	5.2	7.1
n-butane	9.2	12.4	9.7	9.8
iso-butene	9.6	6.8	9.7	10.5
n-butene	3.9	5.0	4.4	4.1
cis-butene	4.8	5.7	5.0	4.9
trans-butene	6.7	7.9	6.8	6.8
iso-pentane	2.5	4.1	4.1	4.8
n-pentane	5.7	4.7	5.4	5.5
1-pentene	0.8	1.0	0.7	0.6
3-methyl-butene	0.3	0.4	0.4	0.5
trans-2-pentene	1.8	2.2	1.9	1.9
cis-2-pentene	5.4	3.6	3.2	3.5
2-methyl-2-butene	6.1	6.0	6.0	5.2
conversion %	1.3	1.3	1.6	2.7

(a) Flow rate 13 ml/min for SAPO's and 56.2 ml/mn for HY
(b) Thermal cracking

Table 5. % conversion in n-octane cracking at 725 K

	1075	1175	1225
Si-0.22	1.7	2.4	~0
LZY-82	> 6	1.5	~0